Nanometer-Resolved Fluidity of Diacrylate Monomers between Silica Surfaces for Sub-15 nm Ultraviolet Nanoimprinting

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論文内容要約

The title of this thesis is “Nanometer-Resolved Fluidity of Diacrylate Monomers between Silica Surfaces for Sub-15 nm Ultraviolet Nanoimprinting”. The author investigated fluidity of diacrylate monomers confined betwe unmodified and modified silica surfaces for sub-15 nm patterning by UV nanoimprinting. Nanometer-resolved surfa characterization methods of surface forces and resonance shear measurements revealed the effects of chemical compositions surfaces and monomers on fluidity in nano-space. The author provided silica templates with sub-15 nm concave holes electron beam lithography, and investigated resin filling behavior into the silica recesses by UV nanoimprinting using t templates.

In the first chapter, the author described a background and an objective of this thesis. UV nanoimprint lithograp (UV-NIL) is one of promising nanofabrication technologies for forefront semiconductor devices because of its high resoluti high throughput, and low cost. The process comprises the following steps: i) pressing a silica mold with nanostructures onto a UV-curable resin film coated on a substrate, ii) filling the mold recesses with the liquid resin, iii) curing the resin by UV light exposure, iv) releasing the mold, v) removing a residual layer of the pattern with the plasma etching process, vi) etching the substrate by using the residual resin as an etching mask, and vii) removing the residual resin to obtain a substrate pattern. Nanostructures at the mold surface are transferred onto the substrate surface by the one-to-one technique. Several demonstrations of sub-15 nm patterning by UV nanoimprinting have been reported in last two decades, whereas fundamental insights based on surface science and chemistry still remain unclear because the recent developments have been achieved by empirical studies. Prof. Nakagawa’s laboratory has been investigating the process in terms of surface science and chemistry. Carbon-coated anodic aluminum oxide (AAO) films with around 20-nm-diameter holes were provided and used in UV nanoimprinting to investigate resin filling behavior into concave recesses. Analysis of the fabricated pillar patterns of UV cured resins indicated that the number of pillars increased with an increase of the number of hydroxy groups in a base monomer. It was found that resin filling into concave recesses with around 20-nm-diameter depended on chemical structures of monomers. From this insight, the author determined to investigate the effects of chemical compositions of surfaces and monomers on

fluidity of monomers confined in nano-space. It is well known that liquid confined between surfaces shows an increase in viscosity near the interface. The increase in viscosity during UV nanoimprinting would have influences on resin filling, horizontal movement of a mold for alignment, and photopolymerization of monomers in nano-space. The objective of this thesis is to reveal fluidity of diacrylate monomers between silica surfaces and to demonstrate sub-15 nm patterning by UV nanoimprinting.

In the second and third chapters, fluidity of diacrylate monomers between silica surfaces was investigated by surface forces and resonance shear measurements. Diacrylate monomers of 1,10-decanediol diacrylate (AC10), dipropenic acid (1-methyl-1,2-ethandiyl)bis[oxy(2-hydroxy-1,3-propanediyl)] ester (70PA), and glycerol 1,3-diglycerolate diacrylate (GDD) were selected in terms of the chemical compositions; AC10 without hydroxy groups, 70PA with two hydroxy groups, and GDD with three hydroxy groups in a monomer structure. Silica sheets cut from flamed silica tubes and glued on cylindrical silica lenses were prepared for the measurements. Silica surfaces modified with chlorodimethyl(3,3,3-trifluoropropyl)silane (FAS3-Cl) or tridecafluoro-1,1,2,2-tetrahydrooctyltrimethoxysilane (FAS13) by chemical vapor surface modification were molecularly smooth enough to carry out the measurements. The FAS3-Cl-modified and FAS13-modified silica surfaces and unmodified silica surfaces treated by vacuum UV light exposure were used for the measurements. The silica sheets glued on silica lenses were mounted on the setup with the cylindrical surfaces faced perpendicularly. The liquid monomer was inserted between the surfaces. The distance (D) between two silica surfaces was determined using fringes of equal chromatic order (FECO) generated by interference of white light between the silver layers deposited on the backside of the silica sheets. We defined the surface distance $D = 0$ for the fluorinated silica surfaces as the contacting probe surfaces in air after surface modification. The surface forces and resonance intensities as a function of the angular frequency were measured upon stepwisely decreasing D and plotted as surface forces curves and resonance curves, respectively. The obtained resonance curves were analyzed using a physical model and viscous parameters b_2 were calculated. The b_2 value of AC10 between unmodified silica surfaces began to increase at $D = 6$ nm and steeply increased at $D < 4$ nm, indicating structuring of monomers confined in nano-space. FAS3-Cl-modified and FAS13-modified silica surfaces increased b_2 values at shorter D than that between unmodified silica surfaces, indicating that the monolayers suppressed the monomer structuring near the interfaces due to weakened intermolecular interactions of monomers and the surfaces. The D between FAS13-modified silica surfaces jumped into contact named as “jump-in” phenomenon in the field of surface forces measurements. It was suggested that FAS13-modified silica surfaces caused thermodynamic instability of monomers confined in sub-10 nm space. These results were consistent with surface forces measurements. The b_2 values of AC10, 70PA, and GDD monomers between unmodified silica surfaces were displayed in the same axis to compare the difference in b_2 values of the monomers. Intriguingly, the b_2 values at $D < 5$ nm and at hard wall showed reverse order in comparison with b_2 in bulk state. This result indicated that hard-wall structuring showed opposite tendency from fluidic structuring. In these chapters, it was revealed that

nanometer-resolved fluidity of liquid monomers depended on the interactions of monomers with surfaces.

In the fourth chapter, the fabrication of silica templates with sub-15 nm concave holes was investigated using electron beam lithography (EBL) involving Ar ion milling. The etching rate of a positive-tone EB resist film in Ar ion beam milling was consistent with the one of a silica substrate. The identical etching rates of the EB resist and silica motivated the author to use the resist layer as an etching mask to silica surfaces. Concave hole patterns on an EB resist film were fabricated by EB spot drawing and subsequent developing. Hole patterns with a diameter of sub-15 nm were observed on the film by field-emission scanning electron microscopy (FE-SEM). The concave patterns were transferred onto a Cr/silica substrate by Ar ion beam milling. Sub-20 nm holes were fabricated, while non-etched defects were generated here and there in the region with a hole diameter of 10 nm. Because the Ar ion beam milling has less anisotropy in etching, we think that Ar ion species has more difficulty to reach to bottom surfaces in the resist holes with a diameter of 10 nm and height of 40 nm. Therefore, the author further investigated how to fabricate silica templates with hole diameters from single digit nanometers by combining Ar ion milling and inductively coupled plasma (ICP) etching. The cross-sectional FE-SEM images showed the vertical concave holes on a silica template. The hole diameters were 20, 15, and 7 nm. Concave holes with sub-15 nm features were fabricated by EBL using Ar ion milling and ICP etching. UV nanoimprinting using the silica template was carried out and the transferred patterns were observed by atomic force microscopy (AFM). Topographic images showed pillar patterns of AC10-based cured resins fabricated using the FAS13-modified silica template. The fabrication of sub-15 nm pillar-like structures were demonstrated, whereas heights of the structures were lower in comparison with hole depths on a silica template.

In the fifth chapter, newly synthesized silicon-containing (meth)acrylates were designed and added into a UV-curable resin to enhance the etching durability to O_2 reactive ion etching (O_2 RIE) for removing a residual layer. The additives were newly designed and synthesized by collaborators because the presence of the phenyl group increases the value of the ring parameter of cured resins and because inorganic silica species generated by the oxidation of such silicon-containing compounds during O_2 RIE improves etching durability. The addition of the additives decreased the etching rate of UV cured films from 42.0 nm min^{-1} to 26.8 nm min^{-1}. The addition of the additives to the base resin improved etching durability to O_2 RIE. Line patterns with a width of 45 nm were fabricated by UV nanoimprinting using the resins without and with the additives. Line breaks and fusion were observed everywhere for imprint patterns made from the resin without additives. It was difficult to maintain line-and-space patterns after O_2 RIE owing to the low etching durability. In contrast, line-and-space imprint patterns remained on a silicon wafer after O_2 RIE in the case of using the resin with additives. It was found that the silicon-containing additives effectively improved etching durability to O_2 RIE for the removal of a residual layer generated after imprinting. However, some line break defects still remained, and the line edge roughness of the resist patterns increased after O_2 RIE. For sub-15 nm UV-NIL, it is necessary to further study how to reduce the line break defects and to maintain the line edge roughness after O_2 RIE. The author proposes that a resin with silicon-containing additives would be available as an etching mask for reverse-tone

UV nanoimprinting.

In this thesis, the nano-rheological properties of diacrylate monomers between fluorinated silica surfaces were evaluated for sub-15 nm patterning by UV nanoimprinting. Sub-15 nm patterning using a silica template with concave holes fabricated by EB lithography was demonstrated, and the resin filling behavior into sub-15 nm silica recesses was discussed considering the nanometer-resolved fluidity of monomers. For sub-15 nm patterning by UV-NIL, the etching durability of UV cured resin films was enhanced by adding silicon-containing additives for etching a residual layer in O_2 RIE with maintaining the pattern size. This thesis provides fundamental insights into the viscosity increases derived from the chemical interactions of the surfaces and monomers and those from among the monomers. The evaluation of the nanometer-resolved fluidity of monomers between unmodified and modified silica surfaces was established, and sub-15 nm patterning, to investigate resin filling into sub-15 nm silica recesses, was demonstrated using a silica template with concave holes fabricated by EBL. The author anticipates that the increase in the monomer viscosity under confinement would affect the fabrication of smaller patterns with sub-15 nm and forefront sub-7 nm features by UV-NIL because the viscosity increase would cause non-fill defects in the mold recesses, a difficulty in moving a mold horizontally for alignment, insufficient curing of resins in the mold recesses, and pull-out defects arising from insufficient curing. To decrease the viscosity confined between the nanospace would be important for sub-15 nm and forefront sub-7 nm patterning by UV nanoimprinting. Further investigation of the nano-rheological properties of UV-curable resins confined between identical and different surfaces are required to overcome the challenge to decrease the viscosity under confinement. The obtained insights reported in this thesis should be helpful for the fabrication of sub-15 nm and sub-7 nm patterns on semiconductor devices to be used by the “big-data society” and in the “Internet-of-Things”.